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EPR, ENDOR and optical spectroscopy of Yb^{3+} ion in $KZnF_3$ single crystals

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ABSTRACT

The paramagnetic center of tetragonal symmetry formed by the Yb^{3+} ion in the $KZnF_3$ crystal has been studied using methods of EPR, ENDOR and optical spectroscopy. The location of the impurity ion and the structural model of the complex differing from the model of the Yb^{3+} center in $KMgF_3$ have been established. The empirical scheme of the energy levels of the Yb^{3+} ion has been found. The parameters of its interaction with the crystal electrostatic field and the hyperfine interaction with ligands of the nearest environment have been determined. The parameters of the crystal field were used for the analysis of the distortions of the crystal lattice in the vicinity of Yb^{3+}. The parameters of the transferred hyperfine interaction have been calculated for the distances between Yb^{3+} and F^- ions of the nearest environment obtained taking into account the found distortions. They are in good agreement with the experimental values.

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1. Introduction

The composition of crystals of double fluorides ($Me^{+}Me^{2+}F_3^-$) with the perovskite-type structure is more complicated than that of, e.g., widely used matrices of the homologous series of fluorite ($Me^{2+}F_2^-$). The high cubic symmetry and a wide variety of physicochemical properties make the study of impurity crystals of double fluorides interesting both from the theoretical and practical point of view.

Using rare-earth (RE) elements as probes makes perovskites useful subjects for studying the behavior of RE ions located in two different positions in the crystal: either in the a-type sites in the environment of the octahedron of six fluorine ions or in b-type sites in the coordination of the same 12 ligands.

However, the introduction of trivalent RE ions in perovskite structures is hampered, on the one hand, by the considerable difference of sizes of RE ions and lattice cations, and on the other hand, by the ion valence of the substitution.

In [1] we presented the results of the detailed study of the tetragonal paramagnetic center of the Yb^{3+} ion in the $KMgF_3$ crystal using electron paramagnetic resonance (EPR), electron-nuclear double resonance (ENDOR) and optical spectroscopy. These results showed conclusively that the tetragonal center is formed during the incorporation of Yb^{3+} in the octahedral positions of Mg^{2+} ions, and not as a result of substituting univalent K^+ ions surrounded by 12 fluorine ions, as it was supposed earlier in [2,3]. The excessive positive charge is compensated by the non-magnetic oxygen ion O^{2-}, which substitutes one of fluorine ions in the octahedron of the nearest environment of the Yb^{3+} ion. One could expect that a similar center would exist in the $KZnF_3$ crystal, the structural parameters of which ($a_0^{KZnF_3}=0.4040$ nm) almost coincide with those of the $KMgF_3$ crystal ($a_0^{KMgF_3}=0.3987$ nm). However, this is not the case in reality. It was found that the tetragonal symmetry center of the Yb^{3+} ion in $KZnF_3$ is formed only upon doping with YbF_3 fluoride and metal lithium. In this work we present the results of the experimental and theoretical study of such Yb^{3+} ion centers in the $KZnF_3$ crystal using methods of EPR, ENDOR and optical spectroscopy.

2. Experimental results

Samples $KZnF_3$:Yb were grown using the Bridgman–Stockbarger method in graphite crucibles in fluorine atmosphere. Crystals were activated by introducing 0.5–1.5 wt% YbF_3 in the charge with the addition of metallic lithium in specific cases. EPR and ENDOR experiments were carried out on modified X-band (9.5 GHz) ERS-231 (Germany) [4] and custom-built EPR/ENDOR X-band spectrometers (see, e.g., [5]) at the temperatures of 4.2 and

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